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DEVELOPMENT OF CHALCOPYRITE CRYSTALS FOR NONLINEAR OPTICAL APPLICATIONS

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I. INTRODUCTION

the authors

With recent results for the optical properties of $CdGeAs_2$ we now know that it meets the expectations of high nonlinearity, phasematchability and transparency in the infrared from 2 μ to 18 μ. When growth problems are solved and larger crack free crystals are obtained, $CdGeAs_2$ should allow the construction of tunable coherent sources over the entire range from 3 μ to 18 μ. In addition, it should allow optimum second harmonic generation of a CO_2 laser to extend its usefulness to 5.3 μ.

This report discusses progress in crystal growth of CdGeAs ~~in section~~ II. ~~In section~~ III the index of refraction data and tuning ranges of the crystal are presented. We also present (as well as) the preliminary nonlinear coefficient measurement results.

These results for $CdGeAs_2$ are now being prepared for a publication which describes the material and its infrared nonlinear applications. Simultaneously, a post deadline paper is being submitted to the CLEA conference in Washington, D.C., in June, 1971.

II. CRYSTAL GROWTH

The equilibrium phase diagram work is nearing completion. Figure 1 shows the Ge-$CdAs_2$ cut through the ternary diagram. The data shows that the range of homogeniety of $CdGeAs_2$ is small which is helpful in obtaining uniform composition single crystal growth. At this time the region near Ge is being completed. The phases shown as Ge + CdGeAs I, II and III have not been identified as yet with crystal structures. X ray work is proceeding toward the understanding of this region of the diagram.

Recently additional growth attempts have been initiated using both the Stockbarger-Bridgeman technique and solution growth at 20% germanium. The solution growth results were not conclusive and indicated that more work is needed. The Bridgeman growth results were encouraging. A recent boule grown according to the prescription given in the last report, gave a single crystal sample over a length of 1 cm which was almost entirely crack free. This substantial improvement in the reduction of cracks seemed to be due to very slow cooling rates. Some cracking in this boule did occur near a twin boundary. The sample was X rayed to determine crystal growth directions on each side of the twin plane. The smaller section of the boule grew nearly parallel to the c axis as has been the case for most previous boules. The larger section grew nearly along a 112 direction. The interest in this particular boule is due to the large disparity in optical transmission for the two sections. The smaller piece was transparent while the large section was cpaque.

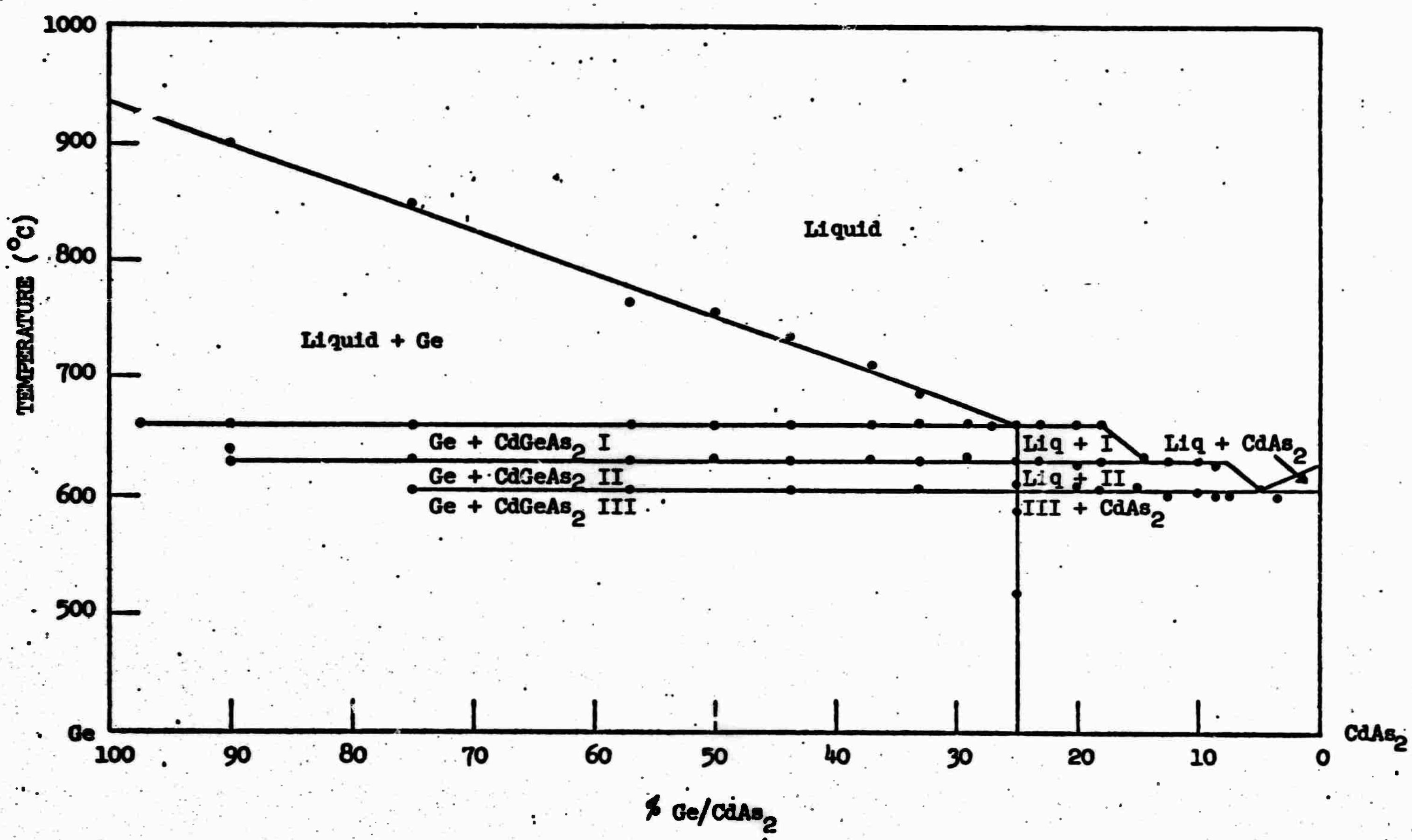


Fig. 1--Equilibrium phase diagram for $CdGeAs_2$ along the Ge-$CdAs_2$ cut.

At this time we expect that a growth direction dependent impurity segregation coefficient may be responsible for the difference in crystal properties. To verify this assumption, mass spectroscopy of each section of the boule is being done. The results should lead to an understanding of the impurity problem for $CdGeAs_2$ and enable work to progress toward the growth of very high quality material.

At this time effort is directed toward the growth of quality single crystals for further optical work. The grown samples are being analyzed for growth direction, optical constants and bulk semiconductor properties. In an effort to obtain highly transparent crystals, work on impurities is being initiated.

III. OPTICAL PROPERTIES OF $CdGeAs_2$

In the last report we described an index of refraction apparatus for use in the infrared. The system has been completed and is in use. It performs as expected making index measurements possible with increased accuracy.

At this time, a few remaining details are being completed. These include laser sources for the visible and infrared and a gas temperature controller for maintaining the crystal at a uniform temperature during measurements.

Using the new high accuracy table, the preliminary index of refraction values given in Table II of the last report have been modified. The new results are shown in Table I.

The index table can read angles to one second. In practice the accuracy of the measured angles is limited by the diffraction effects caused by the finite prism size. With a prism of length L the angular width of the focused beam at the detector is given by

$$\Delta\varphi = 2\,\frac{\lambda f}{LR} \quad , \tag{1}$$

where λ is the wavelength, R is the distance from the center of the table to the detector, and f is the focal length of the focusing optics. For our system we have $R = 23$ cm and $f = 15$ cm . Assuming the detector can be set to the maximum within five percent of the full angular width, we have for a 1 cm prism and a wavelength of 5 µm that the diffraction limits the accuracy of the measured angles to

TABLE I

MEASURED INDICES OF REFRACTION FOR $CdGeAs_2$

λ [μm]	n_e	n_o	$n_e - n_o$
2.88	3.7525	3.6358	0.1167
3.39	3.7285	3.6208	0.1077
4.0	3.7134	3.6124	0.1010
4.43	3.7053	3.6062	0.0991
5.06	3.6953	3.5992	0.0961
10.6	3.6578	3.5688	0.0890

approximately seven seconds.

With the new setup we have remeasured the index of refraction for $CdGeAs_2$. The prism was 4 by 3 mm and had an apex angle of about 13 degrees. The $CdGeAs_2$ has a positive birefringence of about 0.1. For the 3.39 μm and the 10.6 μm points we used laser sources. The other points were taken with a globar light source. Because of the small prism size, the amount of refracted light from the globar was too small for the thermocouple detector at wavelengths larger than five microns. In addition to the low light intensity, the use of a globar light source also requires careful wavelength calibration. We have therefore decided to replace the globar with a laser source. A sealed off He-Xe laser is now under construction which will provide several lines in the infrared. Some of the strongest lines are:[1]

2.027 μ	3.997 μ
2.652 μ	5.357 μ
3.508 μ	5.575 μ
3.680 μ	7.317 μ .

The discharge length is 85 cm and the internal tube diameter is 7 mm. The tube is presently under processing on the vacuum station. As an output coupler we will use a brewster window or a semitransparent gold film on a NaCl substrate. Preliminary testing shows that a film approximately 180 Å thick gives about 4% output coupling at 3 μm decreasing slowly at longer wavelengths.

The indices of refraction in Table I follow from the equation

$$n = \frac{\sin\left(\frac{\alpha + \delta}{2}\right)}{\sin\frac{\alpha}{2}} , \qquad (2)$$

where δ is the minimum deviation angle and α is the apex angle. By differentiating Eq. 2 we obtain

$$\frac{\Delta n}{n} = \frac{1}{2} \cot\!an\left(\frac{\alpha + \delta}{2}\right) \Delta\delta - \frac{1}{2} \frac{\sin \frac{\delta}{2}}{\sin \frac{\alpha}{2} \sin \frac{\alpha + \delta}{2}} \Delta\alpha \; . \qquad (3)$$

With $\alpha \approx 13^{\circ}$ and $\delta \approx 35^{\circ}$, substitution into Eq. 3 yields

$$\frac{\Delta n}{n} \approx 1.1\, \Delta\delta - 3.3\, \Delta\alpha \quad . \qquad (4)$$

The deviation angle was measured ten times and then averaged. We estimate the uncertainty is the deviation angle and the apex angle to be respectively $\Delta\delta = \pm 1'$ and $\Delta\alpha = \pm 1'$. This leads to an estimated uncertainty in our measured indices of $\Delta n = \pm 0.004$.

The index of refraction data in Table I has been used to computer fit a Sellmeier equation for the ordinary and the extraordinary index. The results are

$$n_o^2 = 4.0000 + \frac{8.8910}{1 - \left(\frac{0.5524}{\lambda}\right)^2} + \frac{1.8862}{1 - \left(\frac{36}{\lambda}\right)^2} \qquad (5)$$

and

$$n_e^2 = 4.0000 + \frac{9.5209}{1 - \left(\frac{0.6847}{\lambda}\right)^2} + \frac{1.9087}{1 - \left(\frac{36}{\lambda}\right)^2} \qquad (6)$$

with λ in microns. Under the computer fit the long wavelength resonance was fixed at 36 μm which corresponds to the fundamental phonon absorption band in the material. Figure 2 shows a plot of

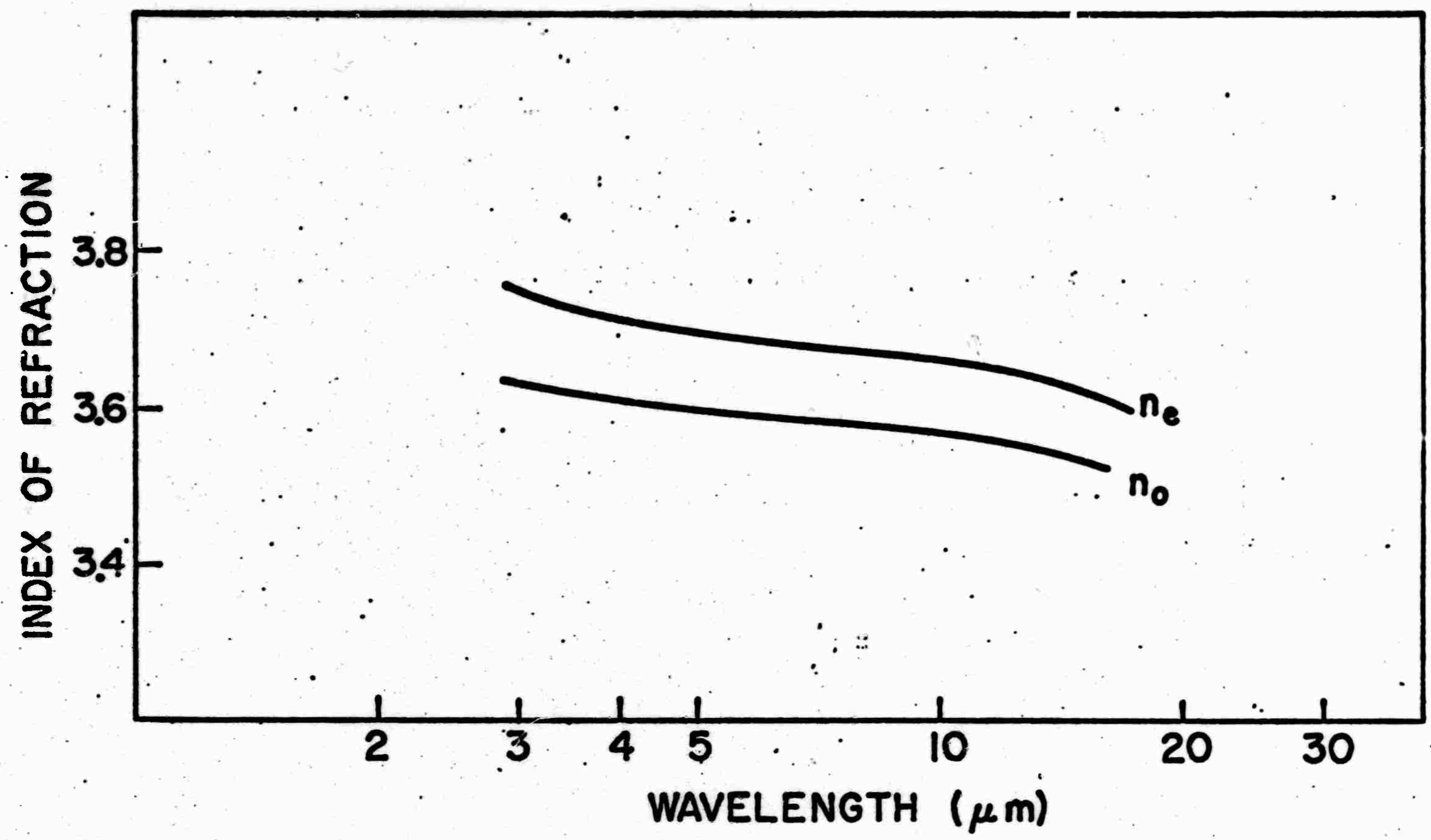


Fig. 2--INDEX OF REFRACTION FOR $CdGeAs_2$

the indices. By taking the limit $\lambda \to \infty$, we can estimate the low frequency dielectric constant. We obtain

$$\epsilon_{\perp} = 14.8$$

$$\epsilon_{\parallel} = 15.4 \quad .$$

The $CdGeAs_2$ has a $\bar{4}2$ m symmetry. The components of the polarization along the principal axis are given by

$$P_x = 2d_{14}E_yE_z$$

$$P_y = 2d_{14}E_zE_x$$

$$P_z = 2d_{36}E_xE_y \quad ; \quad d_{14} = d_{36} \quad .$$

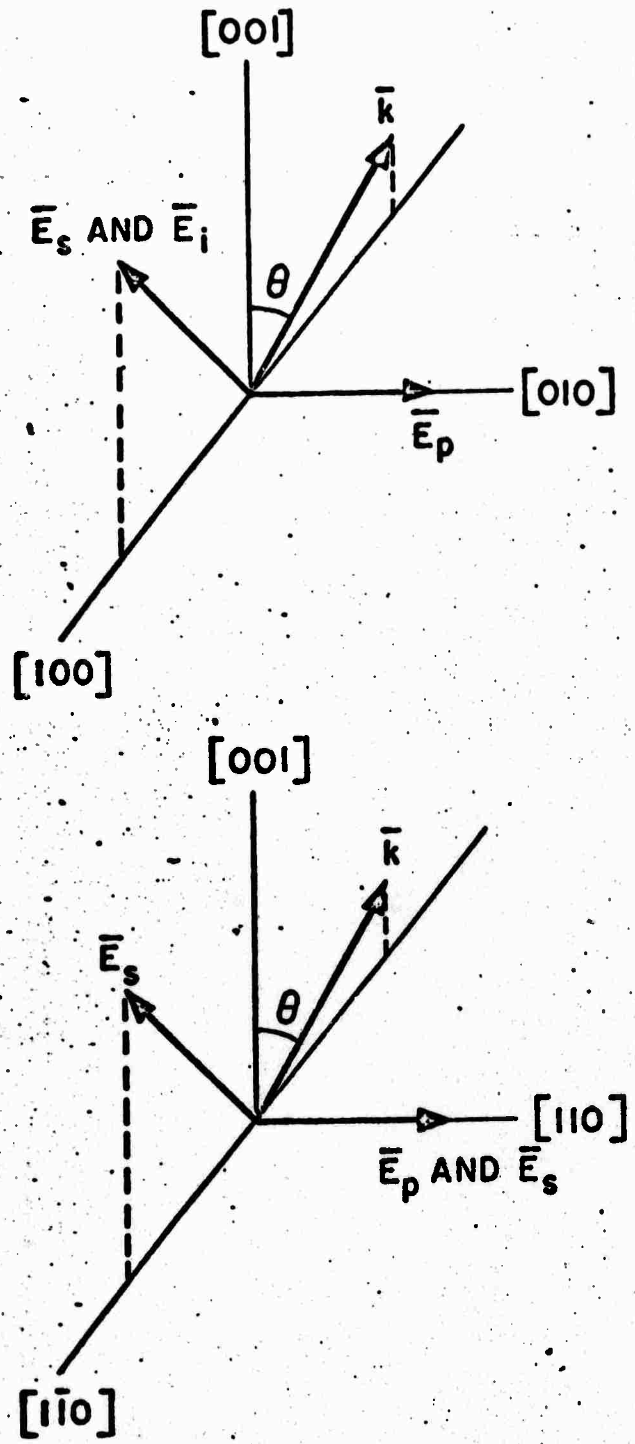
For this crystal symmetry phasematching can be achieved in two different ways. The phasematching conditions can be written as

$$\text{I:} \quad n_p^o\omega_p = n_s^e(\theta)\omega_s + n_i^e(\theta)\omega_i \tag{7}$$

and

$$\text{II:} \quad n_p^o\omega_p = n_s^e(\theta)\omega_s + n_i^o\omega_i \quad . \tag{8}$$

The polarizations and the direction of propagation in the two cases are illustrated in Figs. 3a and 3b. The effective nonlinear coefficients are respectively $d_{14}\sin 2\theta$ and $d_{14}\sin\theta$. Parametric tuning is achieved by crystal rotation. A single crystal can scan approximately 20 degrees. Figures 4 and 5 show tuning curves for several



A

$$n_p^o \omega_p = n_s^e(\theta)\omega_s + n_i^e(\theta)\omega_i$$

$$P_p = 2d_{14} \sin 2\theta \, E_s E_i$$
$$P_s = 2d_{14} \sin 2\theta \, E_i E_p$$
$$P_i = 2d_{14} \sin 2\theta \, E_s E_p$$

B

$$n_p^o \omega_p = n_s^e(\theta)\omega_s + n_i^o \omega_i$$

$$P_p = 2d_{14} \sin \theta \, E_s E_i$$
$$P_s = 2d_{14} \sin \theta \, E_i E_p$$
$$P_i = 2d_{14} \sin \theta \, E_s E_p$$

Fig. 3--PHASE MATCHING IN A POSITIVE BIREFRINGENT CRYSTAL OF $\bar{4}$ 2m SYMMETRY

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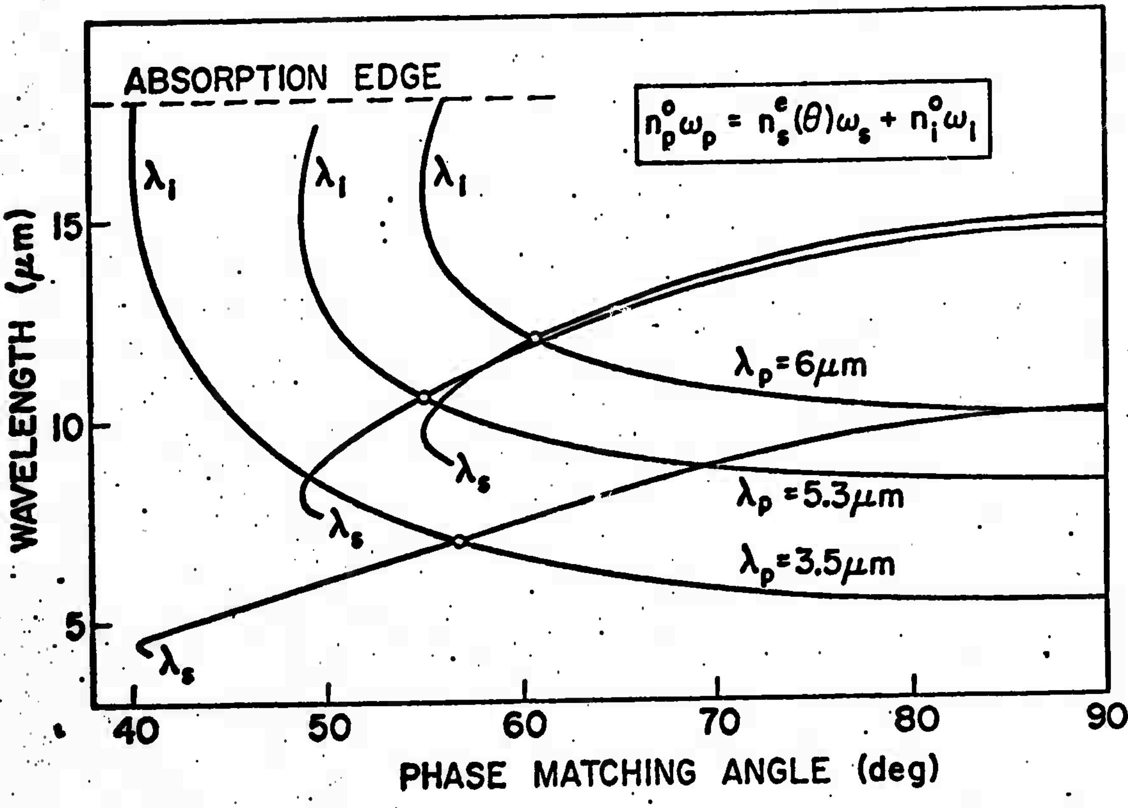

Fig. 4--THEORETICAL TUNING CURVES FOR SEVERAL PUMP WAVELENGTHS IN $CdGeAs_2$

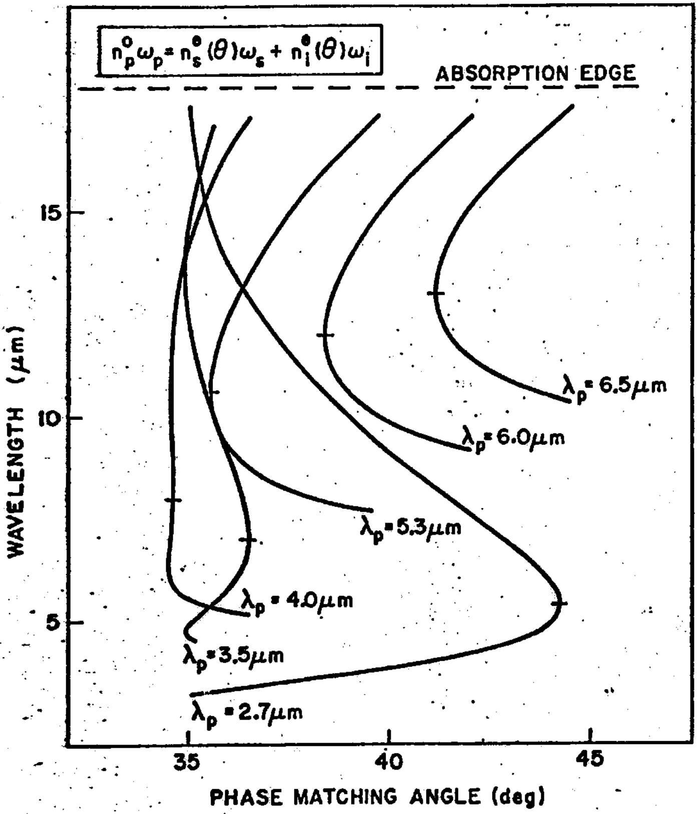

Fig. 5—THEORETICAL TUNING CURVES FOR SEVERAL PUMP WAVELENGTHS IN $CdGeAs_2$

pump wavelengths. Tuning is possible from about 3.5 μm out to the absorption edge at 18 μm. Figures 6 and 7 illustrate the tuning range which can be obtained for a fixed crystal orientation by changing the pump wavelength. The walk-off angle for the extraordinary wave is typically about one degree. A doubled CO_2 laser at 5.3 μm is a potential pump source for infrared parametric oscillators. Figures 8 and 9 show the tuning curves for this particular pump source together with the bandwidths assuming a 1 cm crystal and a narrow pump bandwidth.

Phasematched second harmonic generation (SHG) is possible between 5 and 18 μm for type I phasematching and between 5.4 and 13 μm for type II. Figure 10 shows a plot of the phasematching angle versus wavelength. For doubling of CO_2 the phasematching angles θ and walk-off angles φ are respectively

	θ (deg)	φ (deg)
I	$35^\circ 34'$	$1^\circ 20'$
II	$54^\circ 51'$	$1^\circ 19'$

Type I phasematching is particularly attractive for internal doubling of CO_2 since in that case the fundamental is polarized along one of the optical axis. For type II this is not possible and the crystal birefringence may cause polarization rotation.

Preliminary measurements of the nonlinear coefficient relative to GaAs have been completed. The GaAs sample was Cr doped and had a resistivity of 3×10^8 Ωcm. For the experiment we used a CO_2 laser

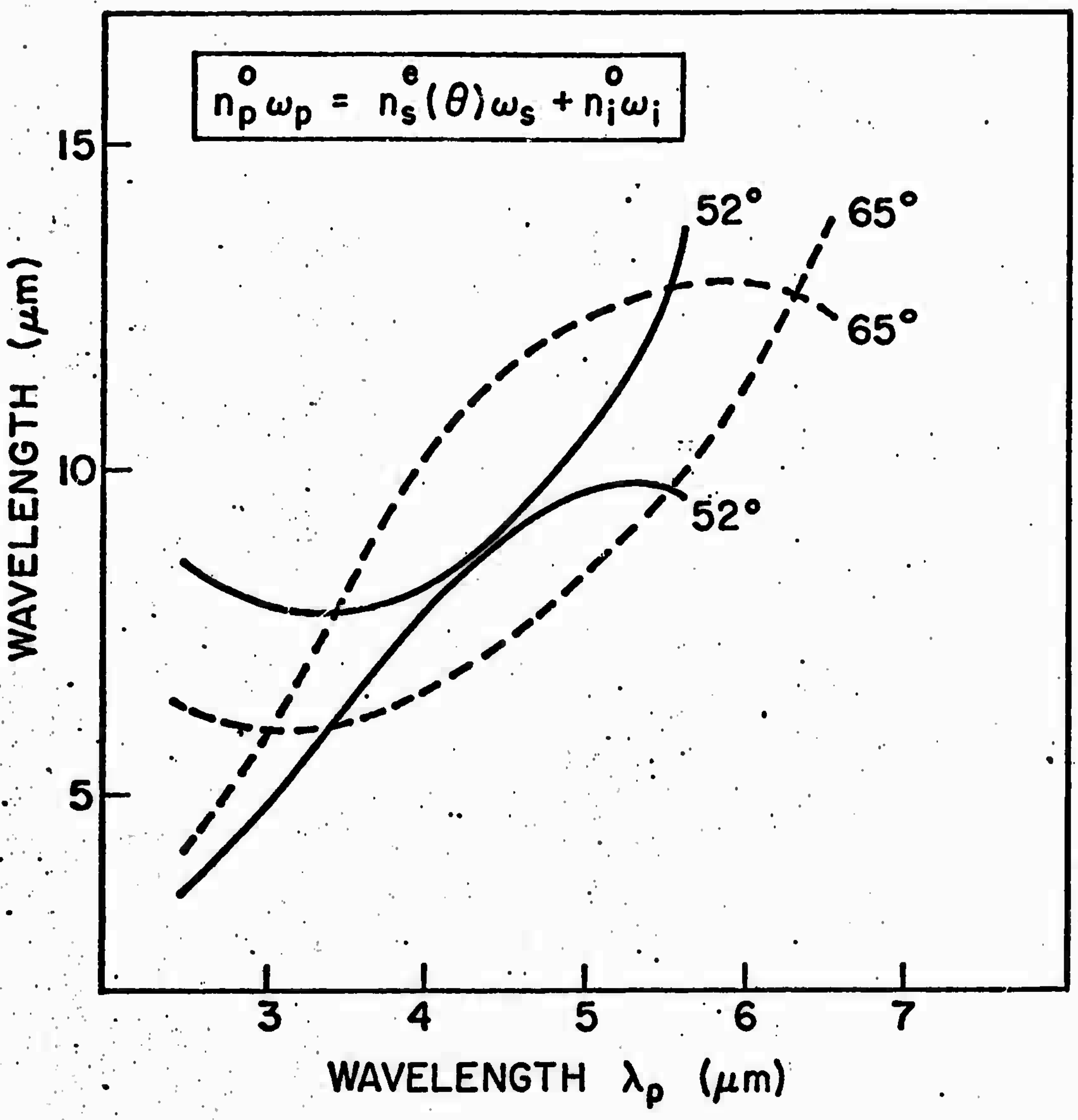

Fig. 6--THEORETICAL TUNING CURVES FOR $CdGeAs_2$ WHEN THE PHASE MATCHING ANGLE IS FIXED

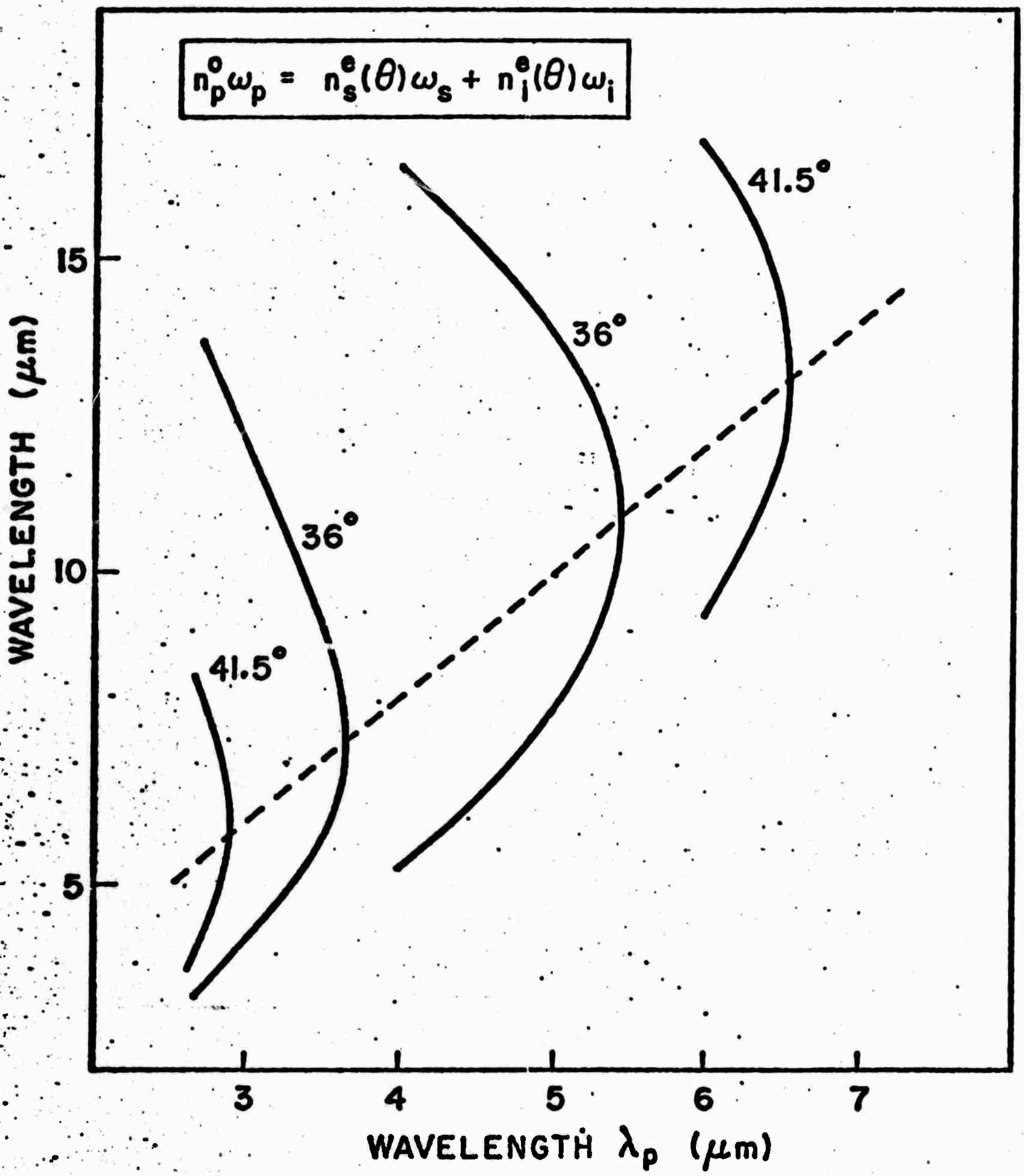

Fig. 7--THEORETICAL TUNING CURVES FOR $CdGeAs_2$ WHEN THE PHASE MATCHING ANGLE IS FIXED

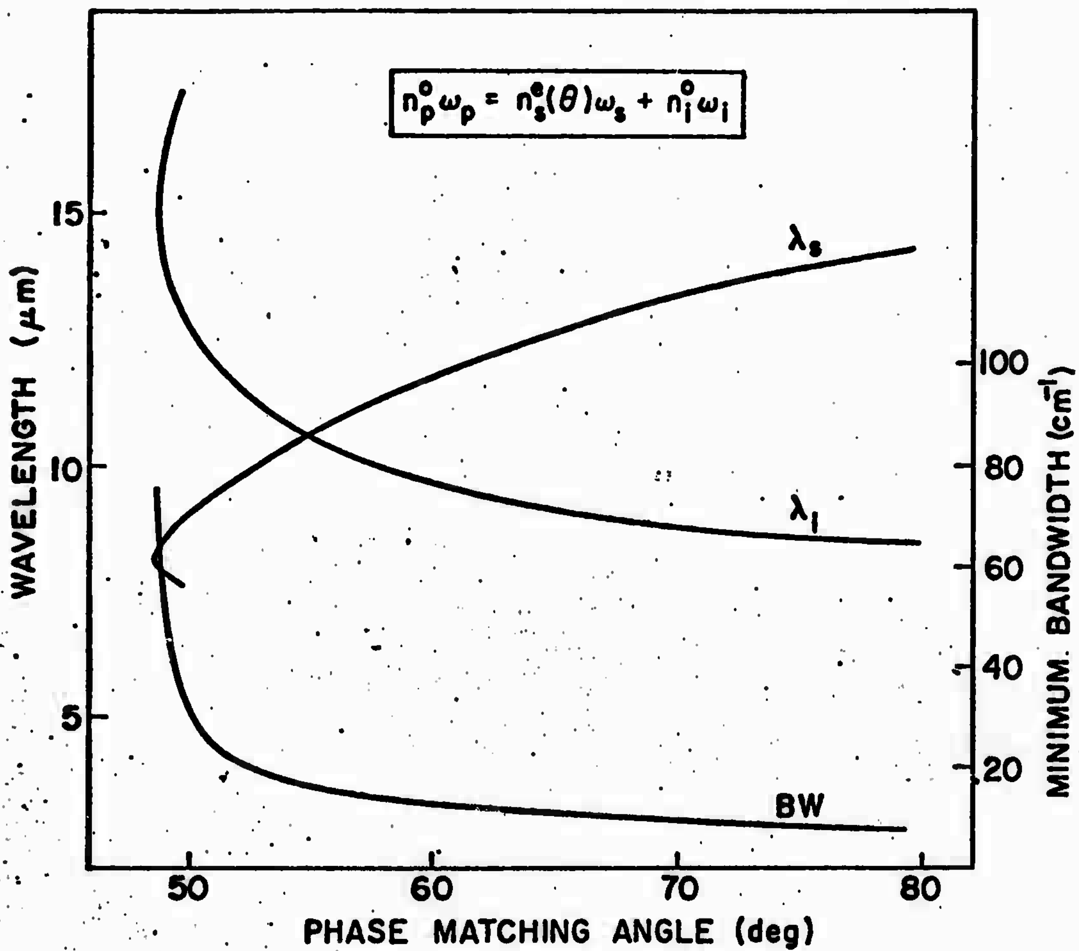

Fig. 8--THEORETICAL TUNING CURVE AND MINIMUM BANDWIDTH FOR A ONE cm $CdGeAs_2$ CRYSTAL PUMPED BY A PUMP WAVELENGTH OF 5.3μm.

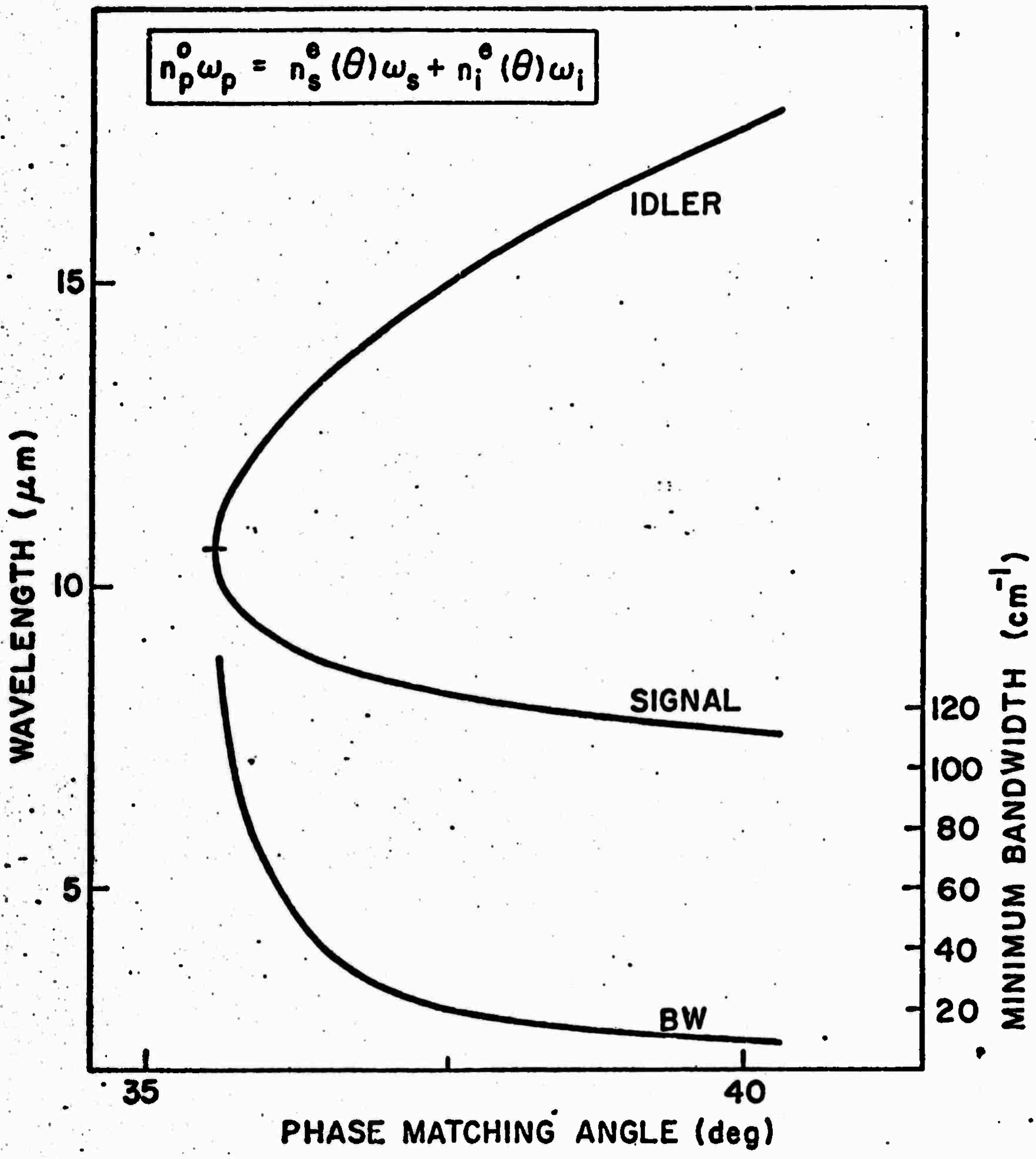

Fig. 9--THEORETICAL TUNING CURVE AND MINIMUM BANDWIDTH FOR A ONE cm $CdGeAs_2$ CRYSTAL PUMPED BY A PUMP WAVELENGTH OF 5.3μm

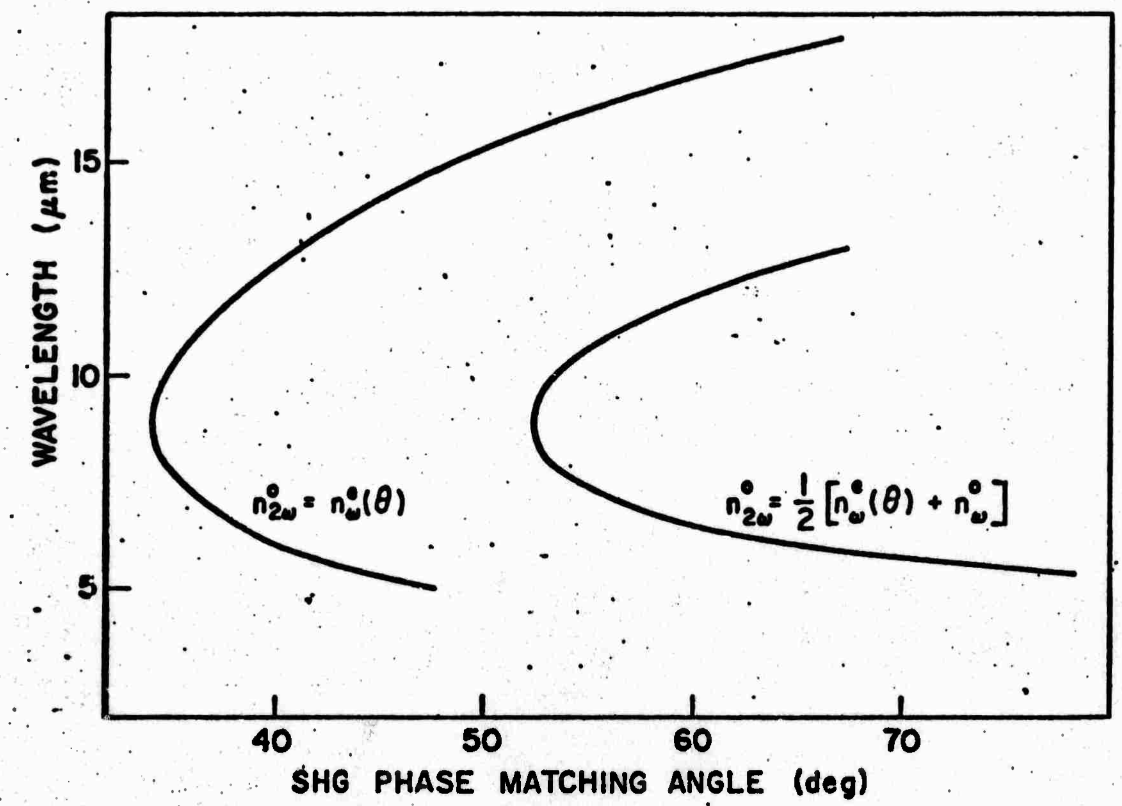

Fig. 10--PHASE MATCHING ANGLE FOR SHG IN $CdGeAs_2$

Q-switched by a rotating grading. The pulse length was about 300-400 nsec and the peak power about 200 Watts. The laser was focused by an uncoated 4 cm Ge lens to a spot size of about 40 μm at the crystal. The $CdGeAs_2$ crystal was polished but uncoated. We did not observe any damage and we estimate the damage threshold to be larger than 2 MW/cm^2 for a Q-switched CO_2 laser. The SHG signal was focused on a liquid nitrogen cooled InSb detector. The detector had a response time of 8 μsec and it did therefore not resolve the pulse, but gave the integrated SHG signal. A pyroelectric detector was used to monitor the CO_2 laser output. The wedged sample technique first proposed by F. F. Wynne and N. Bloembergen[2] was used to measure the nonlinear coefficient. The wedged sample was placed on a micrometer stage and translated through the CO_2 beam. A maximum in the SHG output is observed when the sample thickness is equal to $(2n + 1)\ell_c$ where n is an integer and ℓ_c is the coherence length.

Neglecting absorption, but including reflections at the crystal surface, we have that the SHG power P_2 is related to the fundamental power P_1 at the crystal by

$$P_2 \propto \left\{ \frac{d_{eff} P_1 \ell_c}{(n_2 + 1)(n_1 + 1)^2} \sin\left(\frac{\pi}{2}\frac{\ell}{\ell_c}\right) \right\}^2 , \qquad (9)$$

where ℓ is the crystal thickness and d_{eff} is the effective nonlinear coefficient. When the SHG is maximized, the sine is equal to unity. Table II gives the measured coherence lengths and the maximized SHG powers. The measured coherence length for GaAs agrees well with the published values in Refs. 2 and 3 of respectively

TABLE II

SHG EXPERIMENT

	GaAs	$CdGeAs_2$
Crystal orientation	(111)	(110)
Wedge angle	$4^\circ 58'$	$1^\circ 46'$
CO_2 polarization	∥ [110]	∥ [$1\bar{1}0$]
SHG polarization	∥ [112]	∥ [001]
d_{eff}	$\sqrt{2/3}\, d_{14}$	d_{36}
n_1	3.27[3]	3.5688
n_2	3.30[3]	3.6933
P_1 [rel. units]	1.25	1.3
P_2 [rel. units]	1.1	1.3
ℓ_c [μm]	104 ± 3	22.1 ± 1

104 ± 7 μm and 107 ± 5 μm. For $CdGeAs_2$ we can calculate the expected coherence length using the measured indices of refraction at 10.6 and 5.3 μm. Applying the relation

$$\ell_c = \frac{\lambda}{4(n_2 - n_1)} \quad , \tag{10}$$

we obtain a coherence length of 21.20 μm which is within the experimental error of the measured value.

The nonlinear coefficient relative to GaAs is determined by substituting into Eq. 9. We obtain

$$\frac{d_{36}(CdGeAs_2)}{d_{14}(GaAs)} = 4.9 \quad . \tag{11}$$

According to Miller's rule we would expect

$$\frac{d_{36}(CdGeAs_2)}{d_{14}(GaAs)} \sim 1.8 \quad . \tag{12}$$

The measured nonlinear coefficient for $CdGeAs_2$ therefore appears somewhat large. We had some problems with mode control and laser stability under the measurements, and we plan to repeat the measurements to check our number. We have also tried un-Q-switched SHG. The signal to noise ratio was then about two. Quantitative measurements, however, were difficult because of the 4.3 μm fluorescence from the CO_2 laser. The fluorescence was about four times stronger than the SHG signal. A new 6.6 go 12 μm passband filter

we have just received will solve this problem, however.

In the reported SHG measurements the samples were from boule #16 which is the best boule obtained so far. We have also tested samples from boule #28. This boule has also good optical transmission, but it was quenched from a high temperature to see how quenching affects the crystal cracking. The samples were therefore probably strained with large index inhomogeneities, and we did not obtain good SHG fringes.

We are now looking for two good transparent pieces to cut for type I and type II phasematching to demonstrate the capability of $CdGeAs_2$ as an efficient doubling crystal for CO_2. This will also give us a check on our calculated phasematching angles.

We are also planning to measure the electro-optic coefficients at the HeNe 3.39 μm line. We have two samples from boule #28 cut for the measurements of the r_{63} and r_{44} coefficients. The samples are $4.4 \times 4.0 \times 3.7\ mm^3$ and $3.8 \times 2.1 \times 3\ mm^3$ and with a measured D.C. resistivity at $\varphi_{33} = 88\ \Omega cm$ for the first sample and $\varphi_{11} = 156\ \Omega cm$ for the second. Because of the small resistivities, only small voltages can be applied. To compensate for natural birefringence we have made a quarter-wave plate of $CaMoO_4$ which has a small birefringence of .0054 at 3.39. More experimental details together with the measured coefficients will be present in the next quarterly report.

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